

Weathering Products of Arsenopyrite and Pyrite from El Bollo Mine Wastes (Salamanca, Spain) and their Environmental Hazards

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INTRODUCTION.

Mining and ore processing where tungsten is associated with arsenopyrite (FeAsS) and pyrite (FeS₂) produce As-rich mine wastes. Oxidation of arsenopyrite/pyrite can result in the mobilization and migration of As from these wastes into the environment and the generation of acid mine drainage.

This study considers the arsenopyrite-(pyrite)-rich mine wastes that have undergone about three decades of oxidation in the El Bollo mine. This deposit is located in the NW of the Salamanca province. It is constituted by subvertical quartz-vein swarms with N-S/N10E directions, cutting granites and schists of the Schist-Greywacke Complex. The main minerals present are: scheelite and wolframite, that constitute the ore, and arsenopyrite, pyrite, gold and scorodite (Burkhardt et al. 1987).

The aim of this work is to study the mine wastes from the abandoned tungsten El Bollo exploitation in order to identify and characterise the secondary products generated from arsenopyrite and pyrite weathering, and to assess the potential environmental risk of such wastes.

MATERIALS AND METHODS.

Samples of vein fragments containing quartz, muscovite, sulfides (arsenopyrite, the most abundant, and pyrite) and weathering products (scorodite, Fe (oxyhydr)oxides and native sulfur) were collected. Such vein fragments were studied by X-ray Powder Diffraction (XRD), polarizing microscopy in transmitted and reflected light, and

electron microprobe analysis (EMPA).

In order to assess the environmental risks that may entail the mine wastes present in this area, the subsequent determinations were performed on them: leachability (according to the EN-12457-4 leaching standard) and toxicity (according to the TCLP test method). All the extracts were analysed for As by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

RESULTS AND DISCUSSION

X-ray Diffraction.

XRD analyses were performed on the bulk samples collected from the El Bollo mine wastes and on the yellow greenish and orange-reddish phases distinguished on them. Bulk samples showed scorodite (FeAsO₄·2H₂O), pharmacosiderite (KFe₄(AsO₄)₃(OH)₄(6-7)H₂O) and goethite (α-FeOOH) as secondary minerals, and quartz, muscovite, arsenopyrite and pyrite as primary minerals. The XRD analyses carried out specifically on the yellow-greenish phases revealed that these are mainly composed of scorodite and native sulfur. Goethite, pharmacosiderite and jarosite (KFe³⁺₃(OH)₆(SO₄)₂) were found as the main weathering minerals of the orange-reddish phases.

Polarizing Microscopy.

Microscopically, the following minerals were observed:

- Arsenopyrite appears as unweathered idiomorphic crystals, and from slightly to completely weathered crystals, mostly keeping their original morphology. The arsenopyrite weathering occurs on the

borders, along small cracks, and following the crystallographic planes. Scorodite, native sulphur and Fe (oxyhydr)oxides are the main arsenopyrite weathering minerals, the former being much more abundant. It is very usual to observe corroded relicts of arsenopyrite inside them (fig.1). Scorodite shows different textures: microcrystalline, colloform and prismatic crystals (with size varying from μm to tens of μm) occurring into cavities (fig. 2). Jarosite is observed only in some samples, close to microcrystalline scorodite and in contact with muscovite (fig.3).

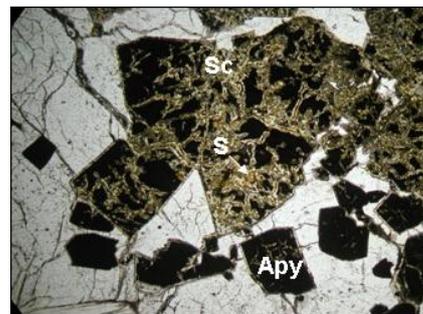


fig 1. Photomicrograph in polarized transmitted light (x4) of arsenopyrite crystals (Apy) weathered to scorodite (Sc) and sulfur (S).

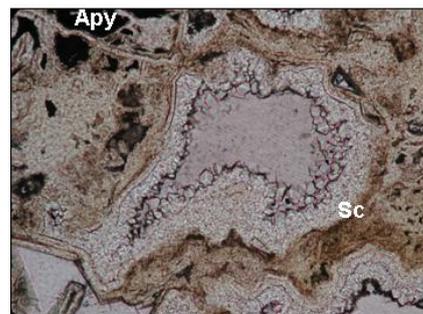


fig 2. Photomicrograph in polarized transmitted light (x10) of scorodite replacing arsenopyrite.

palabras clave: Arsenopirita, pirita, productos de alteración, riesgos medioambientales.

key words: Arsenopyrite, pyrite, weathering products, environmental hazards.

- Pyrite is present as idiomorphic crystals partial or totally replaced by goethite and hydrous ferric oxides (HFO), as pseudomorphs after pyrite. Corroded relicts of pyrite in goethite are frequent.

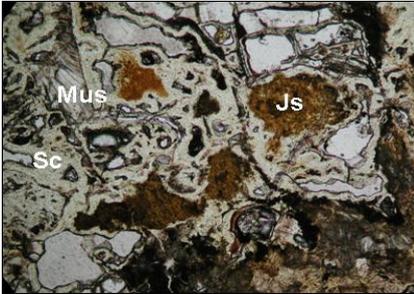


fig 3. Photomicrograph in polarized transmitted light (x10) of jarosite (Js) in scorodite (Sc) and muscovite (Mus).

Electron microprobe analysis.

A total of 175 chemical analyses were performed by EMPA on the observed arsenopyrite and pyrite, and their weathering products: scorodite, native sulphur, goethite, HFO and jarosite.

Arsenic contents in pyrite are below 0.067%wt. Therefore, this mineral is not actually an As source.

The chemical analyses of scorodite reveal that this mineral shows P_2O_5 , SO_3 and PbO contents up to 2.2, 3.9 and 0.5%wt. Also traces of other elements (K, Al, Cu, Zn, Ba) are present. Electron-backscattered images reveal zonation in the colloform scorodite, with darker colors having higher P contents.

The analyses carried out on goethite show Fe_2O_3 and As_2O_5 contents of 72-89.6 and up to 3.46%wt, respectively. The indicated As_2O_5 values agree well with the As(V) adsorption capacities reported in literature for this mineral (García-Sánchez et al., 2002; Lakshminathiraj et al., 2006). Electron-backscattered images show the existence of light grey patches with contents of Fe_2O_3 contents higher than those corresponding to dark grey patches (fig.4).

The chemical composition of HFO shows Fe_2O_3 and As_2O_5 contents comprised, respectively, in the ranges 52.2-62.3 and 9.9-23.1%wt. These phases display much more elevated As adsorption capacities due to their higher number of reactive hydroxyl groups (Pierce and Moore, 1982; García-Sánchez et al., 2002).

Scorodite is considered to be the most

stable phase that immobilizes arsenic whereas the pH is < 3 (Moldovan & Hendry, 2005). When the pH attains values > 3 its incongruent dissolution takes place with the concomitant precipitation of Fe (oxyhydr)oxides and the released As is adsorbed on these neo-formed phases, or occluded in them.

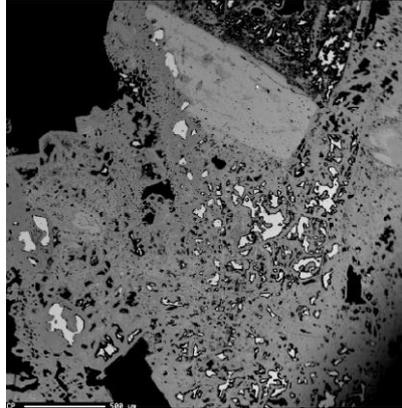


fig 4. Electron backscattered images of Fe (oxyhydr)oxides replacing pyrite crystals (white) with corroded relicts of this mineral.

Jarosite shows K_2O contents varying in a narrow range 6.8-7.7 wt%. Sodium is also present in small amounts (up to 0.4wt% Na_2O). Contents of As_2O_5 are high, between 0.37 and 7.6%wt. In the absence of competitive effects of other anions, K-jarosite presents better removal efficiency than goethite for As(V) (Asta et al., 2009).

Environmental risk assessment.

According to the TCLP test, the As concentrations leached from arsenopyrite and scorodite are 11.2 and 1.3 mg/L, respectively. Therefore, arsenopyrite-bearing mine wastes are classified as toxic because the regulatory limit (5 mg/L) is greatly exceeded. On the other hand, in accordance with the EN-12457-4 leaching standard, the leachable As contents in arsenopyrite and scorodite-bearing mine wastes show values of 157 and 108 mg/kg, respectively. These values greatly exceed the leachable As limit (25 mg/kg) established by the Council Decision 2003/33/EC on waste disposal for the acceptance of wastes at landfills for hazardous wastes.

CONCLUSIONS

Mineralogical studies of the mine wastes from the El Bollo mining area confirm the presence of scorodite,

native sulfur, Fe (oxyhydr)oxides, pharmacosiderite and jarosite (in minor quantity) as secondary minerals. Scorodite, Fe (oxyhydr)oxides and jarosite act as the main mineral scavengers for As, limiting the release and dispersion of this toxic element.

The environmental characterisation of these wastes reveals their toxic or hazardous character, requiring even their treatment for their disposal at landfills for hazardous wastes.

REFERENCIAS

- Asta, M.P., Cama, J., Martínez, M., Giménez, J. (2009): Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications. *J. Hazard. Mater.*, **171**, 965-972.
- Burkhardt, R., García Sánchez, A., Gracia Plaza, A.S. (1987): Mineralizaciones (Sn, W, Au) y control estructural en el Oeste de Salamanca y Zamora. *Cuad. Lab. Xeol. Laxe*, **12**, 289-301.
- Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedure for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. *Off J Eur Communities*, **L11**, 27-49.
- EN-12457-4 (2002): Characterization of waste-leaching-compliance test for leaching of granular waste materials and sludges — Part 4: one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 10 mm (without or with size reduction). Brussels: European Committee for Standardization.
- García-Sánchez, A., Álvarez-Ayuso, E., Rodríguez-Martin, F. (2002): Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils, *Clay Miner.*, **37**, 187-194.
- Lakshminathiraj, P., Narasimhan, B.R.V., Prabhakar, S., Raju, G.B. (2006): Adsorption of arsenate on synthetic goethite from aqueous solutions, *J. Hazard. Mater.*, **136**, 281-287.
- Moldovan, B.J. & Hendry, M.J., (2005): Characterizing and quantifying controls on arsenic solubility over a pH range of 1–11 in a uranium mill-scale experiment. *Environ. Sci. Technol.*, **39**, 4913-4920.
- Pierce, M.L. & Moore, C.B. (1982): Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.*, **16**, 1247-1253.